The synopsis of the proposed research work entitled

Synthesis and characterization of flexible graphene-based electrochemical supercapacitors for storage of electrical energy

To be submitted by

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1. Introduction

Today our society greatly depends on electric and electronic technology. This technology is achieving our needs in past, present and future. There are many expectations from this technology to fulfill our demands. Many materials and techniques are adopted for the development of technology. Graphene is one of the most promising material extensively used in various technologies because of its exceptional features. Applications of graphene will explore sooner and it will be increasing drastically in coming days. Graphene technology is progressing rapidly and even it will replace many predominant materials which are used in current technology in the electric and electronics field. Graphene will solve many problems related with electric energy storage, mechanical strength, and areal capacitance of supercapacitors. Graphene consists sheet of carbon atoms bonded in a honeycomb pattern. Graphene is an allotrope (form) of carbon consisting of a mono layer of carbon atoms and arranged in hexagonal lattice. Graphene is the basic structural element of other forms of carbon like fullerenes, carbon nano tubes, diamond, graphite, charcoal etc. It exhibits electronic mobility 10 times more than silicon. Thus electrical conductivity through graphene is rapid than other conventional electricity conducting materials. The research related theoretical descriptions of graphene likely its composition, structure, and properties resulted in two winning Nobel Prize in Physics in 2010.

Graphene has sparked significant interest due to its ability to store massive amounts of electric charges. Graphene is a transparent and flexible conductor that can be used in various applications like smaller capacitors, completely flexible and even rollable energy-storage devices, transparent batteries with high capacity and fast charging devices. Graphene could establish new generation of energy storage devices not possible with current technology. Graphene has attracted great interest for supercapacitors because of its extraordinary high surface area of up to 2630 m^2g^{-1}. The intrinsic capacitance of single layer graphene was reported to be nearly 21μFcm^{-2} which itself set upper value for electric double-layer capacitance for all carbon –based materials. If the entire surface area can be fully utilized then graphene supercapacitors can achieve capacitance up to 550Fg^{-1}. The maximum density of graphene-based supercapacitors depends on parameters like the thickness, density of graphene film, current collector and the separator, the nature and density of electrolyte, the operating

voltage window of the cell and the packing efficiency. The two key parameters can control the energy density of graphene supercapacitors such as density of graphene film and voltage of the cell. For an electrochemical cell using 200 µm thick graphene electrodes with a density of 1.5 gcm^{-3} and an operating voltage of 4 V, the maximum theoretical energy density is up to 169 $Whkg^{-1}$ on a gravimetric basis and up to 303 Whl^{-1} on volumetric basis. The energy density of graphene supercapacitors achieved so in between 15 to 35 $Whkg^{-1}$ and less than 60 Whl^{-1} which is far less than theoretical values. The performance of graphene electrodes varies between 100 to 1000 $mAhg^{-1}$ depending on the properties of graphene, electrode processing, mass loading, structural defects and surface area. Graphene can be chemically processed in to various forms suitable for both the positive and negative electrodes, enabling the fabrication of an all-graphene battery with an ultra high energy density. Graphene is nice substrate for depositing LIB anode and cathode materials to create high-energy density, flexible, stretchable, fast charging and longer-lasting batteries. In addition to LIBs, graphene hybrids have also been shown to achieve excellent performance in a range of other batteries. Porous graphene composites are also used alternative anode materials to achieve high energy-storage performance.

2. Review of literature and development in the subject

Dean Edwald Von Klesist[1745] developed first capacitor by using large glass bottle, lined on both the side with some type of metal foil. This arrangement is also known as Leyden jar. It was first form of electrical energy (charge) storage. Now days this method is also identified as condensers or capacitors. Then steady research was noted in the field of capacitor technology.

General Electric engineers [1950] designed of capacitors and rechargeable batteries from activated charcoal. It is an electrical conductor that is an extremely porous "spongy" form of carbon with a high specific surface area. H. Becker [1957] developed a "Low voltage electrolytic capacitor with porous carbon electrodes". Donald L. Boos [1970] was registered patent on electrolytic capacitor with activated carbon electrodes. Brian Evans Conway [1975-1980] conducted extensive fundamental and developed work on ruthenium oxide electrochemical capacitors. In [1991] he described the difference between "Supercapacitor" and "Battery" behavior in electrochemical energy storage. With his research, Conway greatly expanded the knowledge of electrochemical capacitors. Using the anode of a 200V high voltage tantalum electrolytic capacitor, David A. Evans [1994]

developed an "Electrolytic-Hybrid Electrochemical Capacitor". These capacitors combine features of electrolytic and electrochemical capacitors. Recent developments include lithium-ion capacitors. These hybrid capacitors were pioneered by FDK in 2007. They combine an electrostatic carbon electrode with a pre-doped lithium-ion electrochemical electrode. This combination increases the capacitance value. Additionally, the pre-doping process lowers the anode potential and results in a high cell output voltage, further increasing specific energy. Research departments actively working in many companies and universities to improve the characteristics of all type of supercapacitors and batteries such as specific energy, specific power, and cycle stability and to reduce production costs.

Now days batteries of smart phones, laptops, mobile banks, tablets and other potable electronic devices have a major problem that battery technology does not kept to the demand placed on them. Reliable battery still has wide range of demand in many electric and electronic applications. Current batteries and supercapacitors are becomes rigid. Hence bending them may cell damage and electrolyte leakage, it loses its mechanical integrity upon bending. 2D one atom thick structure of graphene can adopt mechanical stress shows easily deformation. This flexibility with electrical properties and large surface area makes graphene becomes most promising material having large surface area and used in flexible energy storage.

The present research will focus on wide range of new generations of energy storage devices which has addition of some new features. The summary of this energy storage is as follows:

- *Flexible energy storage devices*
- *Stretchable batteries and supercapacitors*
- *Energy storage devices for wearable electronics*
- *Transparent batteries and supercapacitors*
- *Fast charging lithium-ion batteries*
- *Ultrathin current collectors for lightweight devices*
- *Graphene oxide as solid electrolyte and separator*
- *Supercapacitors with the energy density of batteries*
- *Permselective graphene oxide membrane*
- *Longer-lasting energy-storage devices*
- *Binder and additive-free electrodes*

3. Objectives of research/ proposed hypothesis

The present research work aims at achieving following aims and objectives:

a. *To synthesis Graphene, Graphene Oxide (GO), Reduced Graphene Oxide (RGO) films by Spray Pyrolysis Technique (SPT).*
b. *To study various characteristics techniques of synthesized films of flexible electrochemical graphene based supercapacitors.*
c. *To study electrochemical performance of the graphenesupercapacitor systematically under mechanical deformations.*
d. *To develope superior flexible graphene based materials with 3D structure networks.*
e. *To report the innovative findings beneficial for human beings.*

Hypothesis

- *Developing 3D structured flexible graphene macro-assemblies to minimize the graphene restacking level.*
- *Selection of materials to combine excellent electrochemical performance with good mechanical strength.*
- *To develop high performance of flexible graphene based electrode.*
- *To improve the areal capacitance by graphene films.*

4. Research methodology to be adopted

It is proposed that synthesis of thin films of GO and RGO which can be deposited on sodalime glass substrate by Spray Pyrolysis Technique (SPT). Natural flake Graphite (NFG) can be used for chemical synthesis of Graphene Oxide (GO). SPT is one of the most simple, useful and reliable method to grow graphene oxide thin film. Dimensionality of graphene plays an important role in various applications, and defines properties also. Graphene can be fabricate in the forms structures such as dots(0D), wires (1D), films(2D), monoliths (3D), and self healing or folding (4D). It is observed that 1D, 2D and 3D graphene sheets used in the fabrications of electrodes because it prevents restacking of graphene, thereby leading to supercapacitors with larger specific capacitances. Following Dimensions, shapes, preparation method and applications of graphene can be used in flexible supercapacitors.

Dimensions	*Shapes*	*Synthesis method*	*Applications*
1D Linear structure	*Ribbons*	*Spray Pyrolysis Technique*	*Transparent conducting electrodes, Microscale energy storage devices*

2 D films	*Porous sheets*	*Spray pyrolysis Technique*	*Energy storage and conversion*
3D monoliths	*3D porous films, vertical sheets, honeycomb-like*	*self assembly, Spray Pyrolysis Technique*	*Energy storage.*

We planned to characterize synthesized thin films of graphene by following methods:

1. *Raman Spectroscopy: The structural and chemical bonding of molecules can be characterized by Raman spectroscopy technique.*
2. *X-ray Diffraction (XRD): The presence of functional groups on the sample surface can be determined by XRD technique.*
3. *Scanning Electron Microscopy (SEM): The homogenous coating of grapheme oxide thin film can be observed by SEM technique.*
4. *U-V Visible spectroscopy: The optical absorbance spectrum of GO thin film of nano-sized film can be observed by UV-Visible spectroscopy.*
5. *Four –Point Probe method: Electrical characterization of GO and RGO will be carried out by Four –Point Probe method.*

5. Importance of study/ society applications

Previous research work on the graphene supercapacitors suggests that, the electrode practically used having areal mass loading should be at least 5mgcm^{-2} , with thickness range between 50-200 µm. Our work will try to achieve above standard by incorporating appropriate active materials in graphene electrode. The Spray Pyrolysis Technique (SPT) is famous method for growing a nano materials and fabrication of various sizes of thin films. The films prepared by this technique can be used in wide range of applications such as flexible supercapacitors, gas sensors, solar cells etc. The advantage of this method is that it is simple, effective and low operating cost. The results of characteristic techniques will explain the information about structural and chemical bonding of molecules, presence of functional groups on the sample surface, homogenous coating of graphene oxide, optical absorbance spectrum etc. These results may latter be used in the wide range of advanced electronics, wearable consumable electronics, power cells applications and various upcoming technologies.

6. Proposed work plan/ formulation and structure of study

The tentative scheme of present research work will be as follows:

Sr. No.	*Academic Year*	*Year wise Plan*
1.	*2019-2020*	• *Review of literature and Data Collection* • *Study of related literature* • *Submitting first six monthly report* • *Problem formulation* • *First phase of experimental work (Synthesis of Graphene)* • *Submitting six monthly repot* • *Attending conference on related work*
2.	*2020-2021*	• *Second phase of practical work (Characterization of graphene)* • *Submitting third six monthly report* • *Statistical analysis of data* • *Publication of work in Physics Journals* • *Submitting fourth six month report*
3.	*2021-2022*	• *Third phase of practical work (Enhancement of mechanical strength and areal capacitance of graphene)* • *Submitting fifth six monthly report* • *Attending conference on related work* • *Publication of work in Physics Journals* • *Submitting Sixth six month report* • *Submitting synopsis to SRTMUN, Nanded* • *Submission of thesis*

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